

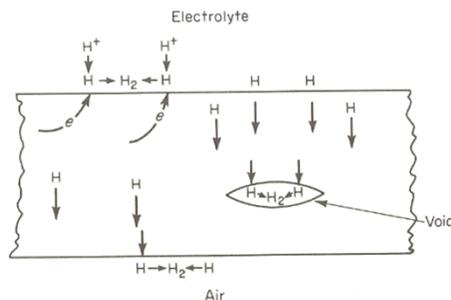
## Other types of corrosion

### 1- Hydrogen damage

Hydrogen damage is a general term which refers to mechanical damage of a metal caused by the presence of, or interaction with, hydrogen. Hydrogen damage may be classified into four distinct types:

#### *a- Hydrogen blistering*

A schematic illustration of the mechanism of hydrogen blistering is shown in following figure. Here, the cross-sectional view of the wall of a tank is shown. The interior contains an acid electrolyte, and the exterior is exposed to the atmosphere. Hydrogen evolution occurs on the inner surface as a result of a corrosion reaction or cathodic protection. At any time, there is a fixed concentration of hydrogen atoms on the metal surface and some of these diffuse into the metal rather than combining into molecules, as shown. Much of the hydrogen diffuses through the steel and combines to form hydrogen molecules on the exterior surface. If hydrogen atoms diffuse into a void, a common defect in rimmed steels, they combine into molecular hydrogen. Since molecular hydrogen cannot diffuse, the concentration and pressure of hydrogen gas within the void increases. The equilibrium pressure of molecular hydrogen in contact with atomic hydrogen is several hundred thousand atmospheres, which is sufficient to rupture any known engineering material.



Schematic illustration showing the mechanism of hydrogen blistering.

### *b- Hydrogen embrittlement*

The exact mechanism of hydrogen embrittlement is not as well known as that of hydrogen blistering. The initial cause is the same, penetration of atomic hydrogen into the metal structure. For titanium and other strong hydride – forming metals, dissolved hydrogen reacts to form brittle hydride compounds. In other materials, such as iron and steel, the interaction between dissolved hydrogen atoms and the metal is not completely known.



### *c- Decarburization*

Decarburization, or the removal of carbon from steel, is often produced by moist hydrogen at high temperature. Decarburization lowers the tensile strength of steel.



### *d- Hydrogen attack*

Hydrogen attack refers to the interaction between hydrogen and component of an alloy at high temperature. A typical example of hydrogen attack is the disintegration of oxygen – containing copper in the presence of hydrogen.

## **2- Biological corrosion**

Corrosive conditions can be developed by living microorganisms as a result of their influence on anodic and cathodic reactions. This metabolic activity can directly or indirectly cause deterioration of a metal by the corrosion process:

1. Produce a corrosive environment
2. Create electrolytic cells on the metal surface
3. Alter the resistance of surface films

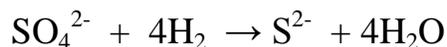
4. Have an influence on the rate of anodic or cathodic reaction
5. Alter the environmental composition

Because this form of corrosion gives the appearance of pitting, it is first necessary to diagnose the presence of bacteria. This is also referred to as microbial corrosion.

The term microorganism covers a wide variety of life forms, including bacteria, blue-green cyanobacteria, algae, lichens, fungi, and protozoa. All microorganisms may be involved in the biodeterioration of metals.

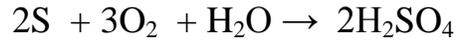
Pure cultures never occur under natural conditions; rather, mixed cultures prevail. Of the mixed cultures, only a few actually become actively involved in the process of corrosion. The other organisms support the active ones by adjusting the environmental conditions to support their growth. For example, in the case of metal corrosion caused by sulfate-reducing bacteria (SRB), the accompanying organisms remove oxygen and produce simple carbon compounds, such as acetic acid and/or lactic acid, as nutrients for SRB. Bacteria are the smallest living organisms on this planet. Some can only live with and others without oxygen. Some can adapt to changing conditions and live either aerobically or anaerobically.

*Anaerobic Bacteria:* Probable the most important anaerobic bacteria which influence the corrosion behavior of buried steel structures are the sulfate – reducing types (*D. desulfuricans*). These reduce sulfate to sulfide according to the following schematic equation:



The source of hydrogen shown in the above equation can be that evolved during the corrosion reaction or that derived from cellulose, sugars, or other organic products present in the soil.

*Aerobic Bacteria:* Aerobic sulfur – oxidizing bacteria, such as thiobacillus thiooxidans, are capable of oxidizing elemental sulfur or sulfur –bearing compounds to sulfuric acid according to the following equation:

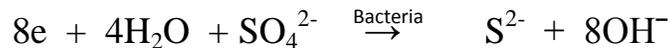


However, in the presence of these bacteria, corrosion can occur without oxygen because the process is different. A number of investigations into the mechanism have been carried out and the most likely explanation of the process is as follows:

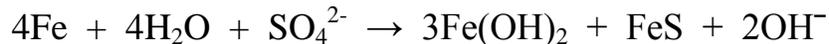
*anodic reaction*



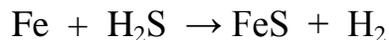
*cathodic reaction*



Combining these equations, the overall reaction is represented as follow:



This represents the corrosion products obtained when bacterial corrosion occurs and is a more likely reaction than the direct one, i.e.



The exact mechanism is not of practical importance but the reaction products indicated above do provide a means of detecting the presence of sulphate-reducing bacteria, which is usually associated with a distinct ‘sulphide’ smell and black corrosion products on the steel. Although sulphate-reducing bacteria do not necessarily attack coatings, they are capable of attacking coated steel if the protective film is porous or damaged.

### **3- Atmospheric corrosion**

Atmospheric corrosion is electrochemical corrosion in a system that consists of a metallic material, corrosion products and possibly other deposits, a surface layer of water (often more or less polluted), and the atmosphere. The general cathodic reaction is reduction of oxygen, which diffuses through the surface layer of water and deposits. The thickness of the water film may have a large effect, but it is more familiar to relate atmospheric corrosion to other parameters. The main factors usually determining the accumulated corrosion effect are time of wetness, composition of surface electrolyte, and temperature.

The parameters that determine time of wetness and composition of surface electrolyte have been surveyed by Kucera and Mattson. They present also a thorough description of the mechanism, with thermodynamic and kinetic aspects of corrosion on various materials. For instance, they consider potential–pH diagrams as a useful thermodynamic basis for understanding atmospheric corrosion. The three main factors, i.e. time of wetness, composition of electrolyte, and temperature, depend for one thing on the type of atmosphere:

- 1.** Rural (inland): dry environment with little or no pollution.
- 2.** Marine: on and by the sea, with high humidity and chlorides.
- 3.** Urban: polluted by exhaust, smoke and soot.
- 4.** Industrial: highly polluted by industry smoke and precipitate.

Climatic conditions are also important. For instance, the corrosion conditions may be severe in the tropical zone due to high temperature and – particularly at the coast – high humidity. However, the picture is not clear. There are also tropical marine atmospheres which are moderately corrosive, and more corrosive atmospheres are found in the typical industrial areas in

the economically developed countries. The ranking also depends on the corroding material.

If the metal surfaces are completely clean and smooth, and there is no pollution of the atmosphere, significant corrosion does not occur at a relative humidity below 100%. In reality, however, materials like steel, copper, zinc and nickel corrode when the relative humidity exceeds 50–70%. This is partly due to corrosion products. Industrial and urban atmospheres contain more or less solid particles consisting of carbon, soot, sand, oxides, and salts, e.g. chloride and sulphate. Many of these substances attract moisture from the air; some of them also attract polluting and corrosive gases.

The salts cause high conductivity, and carbon particles can lead to a large number of small galvanic elements because the particles act as efficient cathodes after deposition on the surface.

Rain affects the corrosion rate in different and opposite ways. Some effects stimulate corrosion, but rain may also wash away pollutants and thus reduce the corrosion rate. The total effect depends on, among other factors, how frequently and heavily it is raining, and on the degree of pollution of the atmosphere. Seldom and heavy rain showers are beneficial. Direct rain on a surface is most favourable at places with strongly polluted atmospheres.

The most significant pollutant in the form of a gas is  $\text{SO}_2$ , originating from combustion of oil, gas or coal containing some sulphur. Together with water,  $\text{SO}_2$  forms sulphuric acid,  $\text{H}_2\text{SO}_4$ . Therefore, metallic materials that corrode strongly in acids are not suitable without a coating in industrial atmospheres with high contents of  $\text{SO}_2$ .

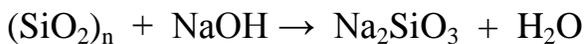
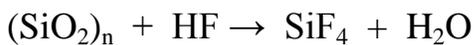
In *marine atmospheres* measured corrosion rates are related to the rates of chloride deposition. Automobile corrosion worries a huge number of people and is of large economic significance. Internal cavities in doors and

nearly closed sections are critical places. This is due to varying temperature and bad ventilation, leading to formation and conservation of condensate, i.e. long time of wetness. In an investigation carried out in Gothenburgh, Sweden, it was found that SO<sub>2</sub> plays a considerable role in the corrosion conditions in internal cavities, while chloride is more significant for the external corrosion of the car. Deposits are strongly polluted, and they attract and preserve moisture. Therefore, a dirty car corrodes continuously most of the time.

#### **4- Corrosion of nonmetallic materials**

##### *a- ceramic*

Ceramic materials consist of compounds of metallic and nonmetallic elements. A simple example is MgO or magnesia. Other ceramics include brick, stone fused silica, stoneware, glass, clay tile, porcelain, concrete, abrasives, mortars, and high – temperature refractories. In general, compared with metals, ceramics resist higher temperatures, have better corrosion and abrasion resistance, including erosion – corrosion resistance, and are better insulators; but the ceramics are brittle, weaker in tension, and subject to thermal shock. Most ceramic materials exhibit good resistance to chemicals, with the main exceptions of hydrofluoric acid and caustic.



##### *b- Cement*

Concrete is the most widely produced material on earth. The use of cement, a key ingredient of concrete, by Egyptians dates back more than

3500 years. In the construction of the pyramids, an early form of mortar was used as a structural binding agent.

In order to understand corrosion damage in concrete, a basic understanding of the nature of concrete as an engineering material is required. It is important to distinguish clearly among terms such as *cement*, *mortar*, and *concrete*.

Unfortunately, these tend to be used interchangeably in household use. The fundamental ingredients required to make concrete are cement clinker, water, fine aggregate, coarse aggregate, and certain special additives. Cement clinker is essentially a mixture of several anhydrous oxides. For example, standard Portland cement consists mainly of the following compounds, in order of decreasing weight percent:  $3\text{CaO}.\text{SiO}_2$ ,  $2\text{CaO}.\text{SiO}_2$ ,  $3\text{CaO}.\text{Al}_2\text{O}_3$ , and  $4\text{CaO}.\text{Al}_2\text{O}_3.\text{Fe}_2\text{O}_3$ . The cement reacts with water to form the so-called cement paste. It is the cement paste that surrounds the coarse and fine aggregate particles and holds the material together. The importance of adequately mixing the concrete constituents should thus be readily apparent. The fine and coarse aggregates are essentially inert constituents. In general, the size of suitable aggregate is reduced as the thickness of the section of a structure decreases.

The reaction of the cement and water to form the cement paste is actually a series of complex hydration reactions, producing a multiphase cement paste. One example of a specific hydration reaction is the following:



Following the addition of water, the cement paste develops a fibrous microstructure over time. Importantly for corrosion considerations, the cement paste is not a continuous solid material on a microscopic scale.

Rather, the cement paste is classified as a “gel” to describe its limited crystalline character and the water-filled spaces between the solid phases.

These microscopic spaces are also known as gel “pores” and, strictly speaking, are filled with an ionic solution rather than “water.” Additional pores of larger size are found in the cement paste and between the cement paste and the aggregate particles. The pores that result from excess water in the concrete mix are known as capillary pores. Clearly then, concrete is a porous material, and it is this porosity that allows the ingress of corrosive species to the embedded reinforcing steel. A further important feature of the hydration reactions of cement with water is that the resulting pore solution in concrete is highly alkaline. In addition to calcium hydroxide, sodium and potassium hydroxide species are also formed, resulting in a pH of the aqueous phase in concrete that is typically between 12.5 and 13.6.

Under such alkaline conditions, reinforcing steel tends to display completely passive behavior, as fundamentally predicted by the Pourbaix diagram for iron. In the absence of corrosive species penetrating into the concrete, ordinary carbon steel reinforcing thus displays excellent corrosion resistance.

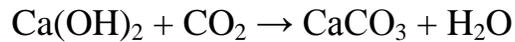
From the above discussion, the complex nature of concrete as a particulate- strengthened ceramic-matrix composite material and the difference between the terms *concrete* and *cement* should be apparent.

*Corrosion mechanisms:* The two most common mechanisms of reinforcing steel corrosion damage in concrete are (1) localized breakdown of the passive film by chloride ions and (2) carbonation, a decrease in pore solution pH, leading to a general breakdown in passivity.

Harmful chloride ions usually originate from deicing salts applied in cold climate regions or from marine environments/atmospheres. Carbonation

damage is predominantly induced by a reaction of concrete with carbon dioxide (CO<sub>2</sub>) in the atmosphere.

Carbon dioxide present in the atmosphere can reduce the pore solution pH significantly by reacting with calcium hydroxide (and other hydroxides) to produce insoluble carbonate in the concrete as follows:



Carbonation is manifested as a reduction in the pH of the pore solution in the outer layers of the concrete and often appears as a well defined “front” parallel to the external surface. This front can conveniently be made visible by applying a phenolphthalein indicator solution to freshly exposed concrete surfaces. Behind the front, where all the calcium hydroxide has been depleted, the pH is around 8, whereas ahead of the front, the pH remains in excess of 12.5 . The passivating ability of the pore solution diminishes with the decrease in pH. Carbonation-induced corrosion tends to proceed in a more uniform manner over the rebar surface than chloride-induced corrosion damage.

### **High – temperature corrosion (oxidation)**

Although oxidation generally refers to an electron producing reaction, this term is also employed to designate the reaction between a metal and air or oxygen in the absence of water or an aqueous phase.

Pilling and Bedworth proposed that oxidation resistance should be related to the volume ratio of oxide and metal. Mathematically, this can be expressed as:

$$P.B.R = \frac{W_d}{D_w}$$

where  $W$  is the molecular weight of the oxide,  $w$  is the atomic weight of the metal,  $D$  and  $d$  are the specific densities of the oxide and metal respectively. The ratio  $R$  indicates the volume of oxide formed from a unit volume of metal. According to Pilling and Bedworth, a volume ratio of less than 1 produces insufficient oxide to cover the metal and is unprotective.

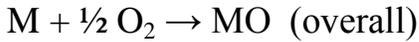
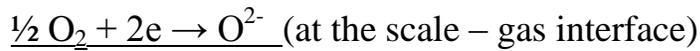
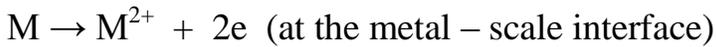
The volume ratios for some metals are listed in following table. As shown, this ratio does not accurately predict oxidation resistance, although there is some qualitative agreement. In general, metals with volume ratios of less than 1 form nonprotective oxides, as do those with very high volume ratios (2 to 3).

Oxide – metal volume ratios

Protective oxides		Nonprotective oxides	
Be	1.59	Li	0.57
Cu	1.68	Na	0.57
Al	1.28	K	0.45
Si	2.27	Ag	1.59
Cr	1.99	Cd	1.21
Mn	1.79	Ti	1.95
Fe	1.77	Mo	3.61
Co	1.99	Cb	2.61
Ni	1.52	Sb	2.35
Pd	1.60	W	3.40
Pb	1.40	Ta	2.33
Ce	1.16	U	3.05
		V	3.18

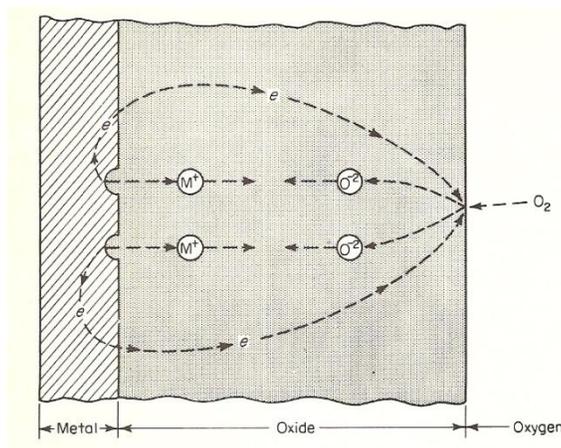
### ***Electrochemical and Morphological Aspects of oxidation***

Oxidation by gaseous oxygen, like aqueous corrosion, is an electrochemical process. It is not simply the chemical combination of metal and oxygen,  $M + \frac{1}{2} O_2 \rightarrow MO$ , but consist of two partial processes:



with new MO lattice sites produced either at the metal – scale interface or at the scale – gas interface.

Gaseous oxidation may be considered as analogous to aqueous galvanic corrosion. Metal ions are formed at the metal – scale interface and oxygen is reduced to oxygen ions at the scale – gas interface. Because all metal oxides conduct both ions and electrons to some extent, this electrochemical reaction occurs without the necessity of an external electronic conductor between the local anode and the local cathode. Viewing following figure, it can be seen that the oxide layer serves simultaneously as (1) an ionic conductor (electrolyte), (2) an electronic conductor, (3) an electrode at which oxygen is reduced, and (4) a diffusion barrier through which ions and electrons must migrate.

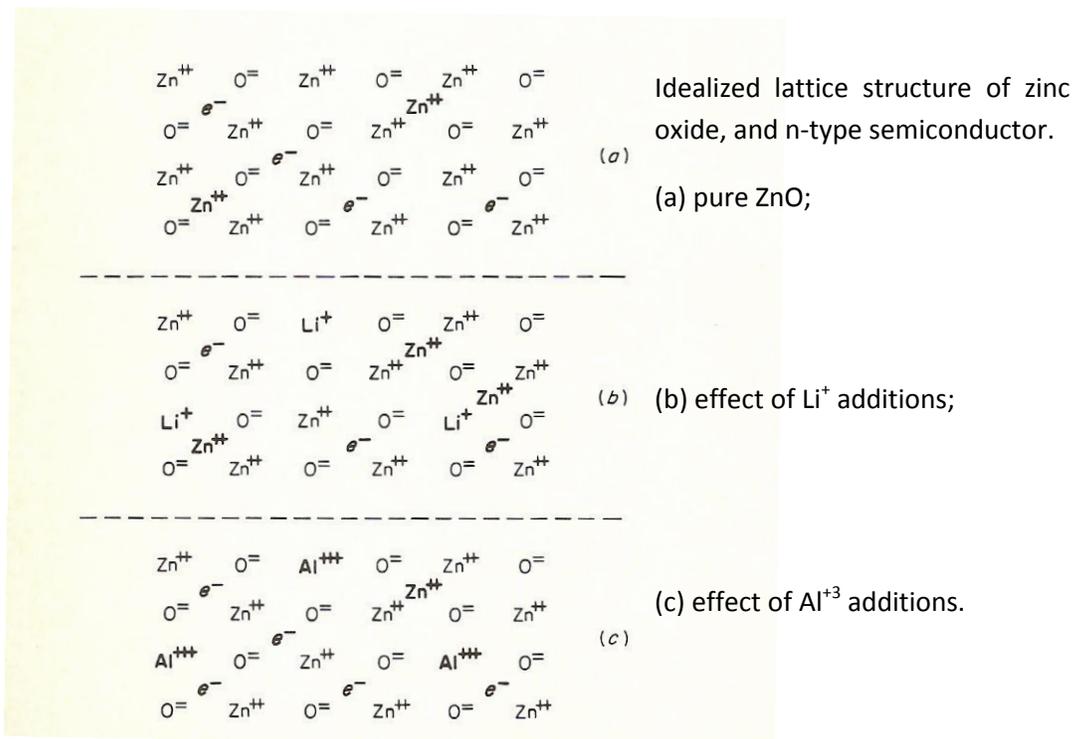


Many metal – oxygen phase diagrams indicate several stable binary oxides. For example, iron may form the compounds FeO, Fe<sub>3</sub>O<sub>4</sub>, and Fe<sub>2</sub>O<sub>3</sub>; copper may form Cu<sub>2</sub>O and CuO; etc.

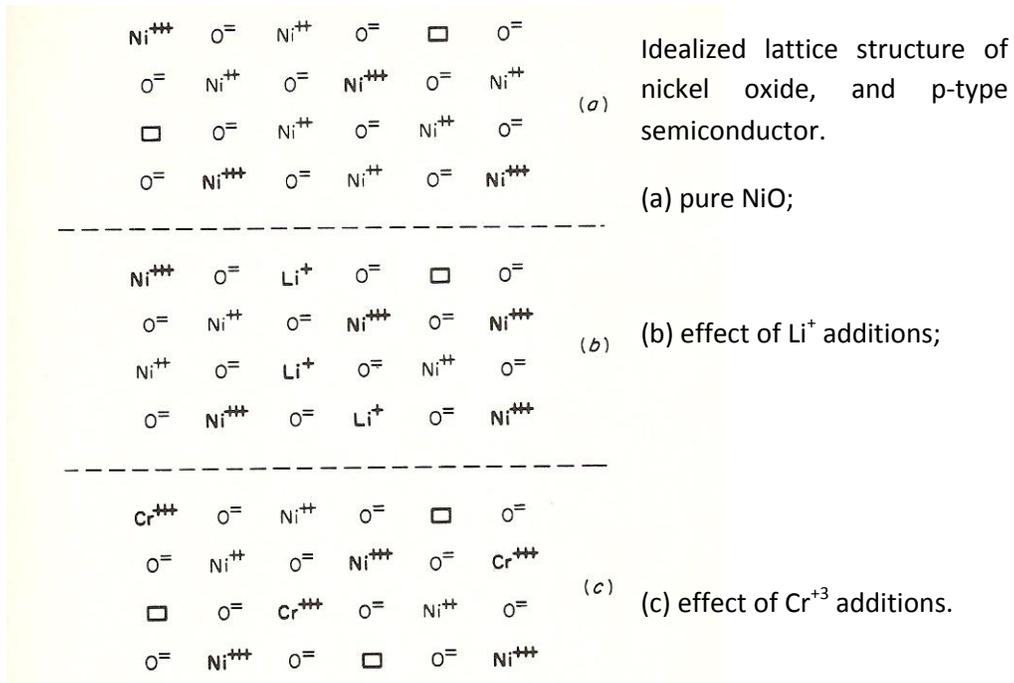
**Oxide Defect Structure**

Illustration (a) in following figure schematically shows a metal – excess oxide – zinc oxide, ZnO. In this representation, two extra zinc ions occupy interstitial lattice positions; four excess electrons are also present for electroneutrality. In this structure, electronic current is carried by the excess electrons and ionic transport by the interstitial zinc ions. Zinc oxide is termed an *n* – type semiconductors since it contains an excess of negatively charged electronic current carriers (electrons).

Other *n* – type semiconducting oxides include: CdO, TiO, Ta<sub>2</sub>O<sub>5</sub>, Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, Cb<sub>2</sub>O<sub>5</sub>, and PbO<sub>2</sub>. However, of this group, at least Ta<sub>2</sub>O<sub>5</sub> and Cb<sub>2</sub>O<sub>5</sub> are metal – deficient, with oxygen vacancies as the predominant ionic defect.



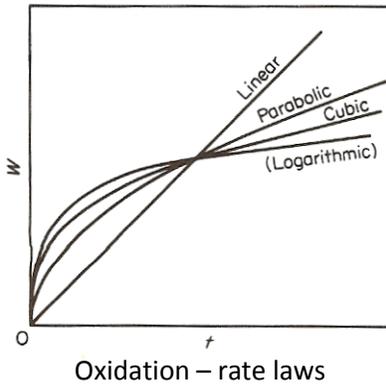
Nickel oxide, NiO, shown in following figure (a) is a metal – deficient oxide. In this structure, vacant metal ion sites (vacancies) are denoted by squares. Also, for each nickel ion vacancy there are two trivalent nickel ions in normal lattice positions. These trivalent ions can be considered as a divalent ion and an associated “electron hole” (or absence of an electron). Electronic conduction occurs by the diffusion of these positively charged electron holes and, hence, this oxide is termed a *p* – type semiconductor. Ionic transport occurs by the diffusion of the nickel vacancies. Other oxides of this type are FeO, Cu<sub>2</sub>O, Cr<sub>2</sub>O<sub>3</sub>, and CoO.



### ***Oxidation Kinetics***

The most important parameter of metal oxidation from an engineering viewpoint is the reaction rate. Since the oxide reaction product is generally retained on the metal surface, the rate of oxidation is usually measured and expressed as weight gain per unit area. The various empirical rate laws

sometimes observed during oxidation for various metals under various conditions are illustrated in following figure, in which a plot of weight gain per unit area versus time is shown.



The simplest empirical relationship is the linear law

$$W = k_L t$$

where W is weight gain per unit area, t is time, and  $k_L$  is the linear rate constant.

In 1933, C.Wagner showed that the ideal ionic diffusion – controlled oxidation of pure metals should follow a parabolic oxidation rate law,

$$W^2 = k_p t + C$$

where W is weight gain per unit area, t is time,  $k_p$  is the parabolic rate constant, and C is a constant.

The logarithmic empirical reaction rate law

$$W = k_e \log(Ct + A)$$

where  $k_e$ , C, A, are constant, and the related inverse logarithmic oxidation rate law

$$\frac{1}{w} = C - k_i \log t$$

where  $k_i$  and  $C$  are constants, do not differ greatly because data usually fit both equations equally satisfactorily.

Under specific conditions, some metals appear to oxidize according to a cubic law

$$W^3 = k_c t + C$$

where  $k_c$  and  $C$  are constants, or according to some other rate law with exponents different from 3 (e.g., 2.5, 3.4, etc).

## **The Factors Affecting on The Corrosion Rate**

### ***1- Metallurgical factors***

The Structure and Composition of both metals and alloys are important in deciding their corrosion characteristics. Indeed, structure and composition are critical in many forms of localized corrosion. For a metal or alloy to corrode evenly, the anodic and cathodic sites must be interchangeable. This implies that every site on the surface is energetically equivalent and therefore equally susceptible to dissolution, but this is never the case.

### ***Metals and Metal Surfaces***

Metals form as a series of irregular crystals. If these crystals or grains were perfect, the metal atoms would lie in regular close-packed planes. If this were true, the rate of metal dissolution would depend on which crystallographic planes were exposed to the corrosive environment.

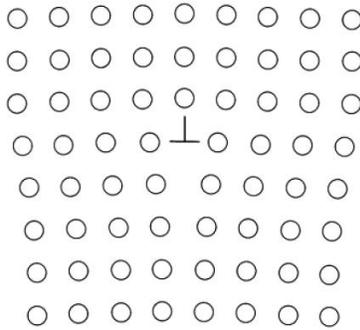
In addition to these perfect features, there are many sources of atomic disarray within the crystals that can lead to defects where they emerge at the surface. Some of the more significant crystal defects are described below.

**Stacking Faults.** The atoms in metals form close-packed layers that stack in various sequences. The most common crystal structures found in metals are

the body-centered cubic (bcc), the face-centered cubic (fcc), and the hexagonal close-packed (hcp). If the crystal structures are mixed, resulting in an error in the normal sequence of stacking of atomic layers, stacking faults are produced. These faults can extend for substantial distances through, and across, the crystal.

**A slip plane** is the lattice plane separating two regions of a crystal that have slipped relative to each other. Such permanent displacements occur under the influence of plastic deformation.

**Dislocations.** Slip regions can be caused by the movement of various small lattice dislocations, such as an additional layer of atoms or a stacking fault on one side of the defect. Dislocations are defects that exist in nearly all real crystals. An edge dislocation, which is the edge of an incomplete plane of atoms within a crystal, is shown in cross section in following figure. In this illustration, the incomplete plane extends partway through the crystal from the top down, and the edge dislocation (indicated by the standard symbol ) is its lower edge.



Schematic of a section through on edge dislocation,  
which is perpendicular to the plane of the  
illustration and is indicated by the symbol.

**Point defects** may be vacancies caused by the absence of one or more atoms in the crystal, impurity atoms of different sizes, and interstitial atoms (small atoms in spaces between the lattice atoms). Point defects can affect significant volumes of the crystal.

**Grain Boundaries.** The interface between grains is termed the grain boundary, and it is a region of major atomic disarray at which many faults and dislocations congregate. This disarray makes it energetically easier for impurities to concentrate at grain boundaries as opposed to the grain interior, where the atomic arrangement is more regular.

### ***Effect of Alloying on Corrosion Resistance***

Pure metals have a low mechanical strength and are rarely used in engineering applications. Stronger metallic materials, which are combinations of several elemental metals known as alloys, are most often used. Commonly used alloys have a good combination of mechanical, physical, fabrication, and corrosion qualities. The specific applications determines which of these qualities is deemed most important for alloy selection.

Alloys can be single phase or polyphase, depending on the elements present and their mutual solubilities.

One of the primary reasons for producing alloyed, or stainless, steels is to improve corrosion resistance. Alloying can affect corrosion resistance in many different ways.

**Increased Nobility.** Alloying can have a genuinely thermodynamic effect on corrosion resistance by increasing the nobility of the material. This is achieved by a decrease in  $\Delta E_{\text{therm}}$ , which is expressed by following equation and illustrated in the Evans diagram.

$$\Delta E_{\text{therm}} = (E_e)_c - (E_e)_a$$

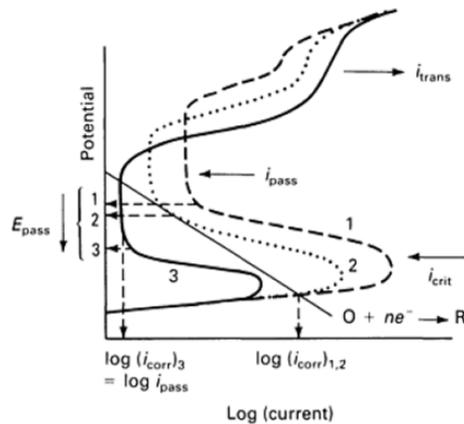
where  $E_e$  is the equilibrium corrosion potential for cathodic c and anodic a reaction.

Noble systems of this intermetallic type are rare and generally produced only when the alloying element is a noble metal, such as gold, platinum, or palladium. For such alloys, the less noble constituent metal, for example, titanium in a Ti-2Pd alloy, often dissolves preferentially, leaving a protective film of noble metal on the alloying surface. Disruption of this surface film, which is often thin, will reinitiate corrosion.

**Formation of a Protective Film.** The addition of controlled amounts of selected alloying elements can often improve the stability and protectiveness of surface oxide films formed on the material surface. Thus, the addition of chromium to iron has a major effect on the corrosion resistance in acid.

This can be appreciated by studying the anodic polarization curves for iron-chromium alloys shown in following figure, where the curves exhibit an active-passive transition.

The addition of chromium leads to decreases in the critical current for passivation ( $i_{crit}$ ), the passivation potential ( $E_{pass}$ ), and the passive current ( $i_{pass}$ ), as indicated by the arrows in figure. Therefore, for the cathodic reaction shown, passivation is achievable only in case 3 for a steel containing more than approximately 12% Cr. The improved resistance to corrosion is due to an increase in chromium content of the iron chromium oxide layer formed on the alloy surface.



Schematic anodic polarization diagrams for stainless steels containing various amounts of chromium. (1) 3%Cr; (2) 10%Cr; (3) 14%Cr.

## 2- Environmental factors

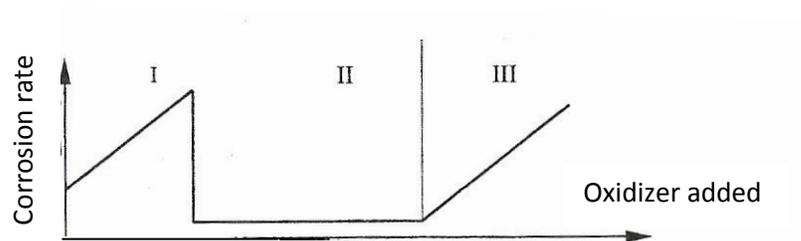
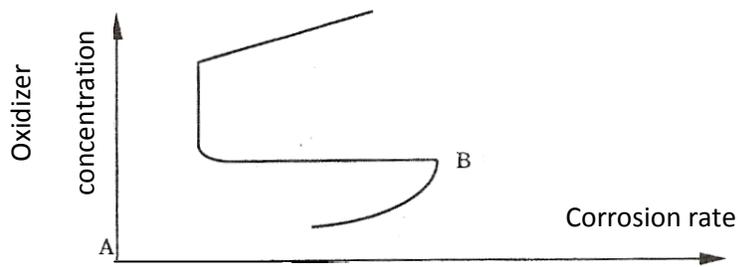
### Effect of oxygen and oxidizers

The effect of oxidizers and oxidizing power was discussed through the behavior of active – passive metals. The effect of oxidizers on corrosion rate can be represented by the graph shown in following figure. Note that shape of this graph is similar to that of polarization curve and that this figure is divided into three different sections. Behavior corresponding to section I is characteristic of normal metals and also of active – passive metals when they exist only in the achieved only if a sufficient quantity of oxidizer or a sufficiently powerful oxidizer is added to the medium.

If an active – passive metal is initially passive in a corrosive medium, the addition of further oxidizing agents has only a negligible effect on corrosion rate. The behavior represented by sections II and III results when a metal, initially in the passive state, is exposed to very powerful oxidizers and makes a transition into the transpassive region.

It is readily seen that the effect of oxidizer additions or the presence of oxygen on corrosion rate depends on both the medium and the metals involved.

The corrosion rate may be increased by the addition of oxidizers, oxidizers may have no effect on the corrosion rate, or a very complex behavior may be observed. By knowing the basic characteristics of a metal or alloy and the environment to which it is exposed, it is possible to predict in many instances the effect of oxidizer additions.



I+II+III	II+III	II	I+II	I
-18Cr+8Ni in HNO <sub>3</sub> +H <sub>2</sub> SO <sub>4</sub> mixture at elevated temp.	-18Cr+8Ni in HNO <sub>3</sub> +Cr <sub>2</sub> O <sub>3</sub>	-18Cr+8Ni in HNO <sub>3</sub> -Hastelloy in FeCl <sub>3</sub>	-18Cr+8Ni in H <sub>2</sub> SO <sub>4</sub> +Fe <sup>+2</sup> -Ti in Cu <sup>+2</sup> +HCl	-Monel in O <sub>2</sub> +HCl -Cu in O <sub>2</sub> +H <sub>2</sub> SO <sub>4</sub> -Fe in O <sub>2</sub> +H <sub>2</sub> O

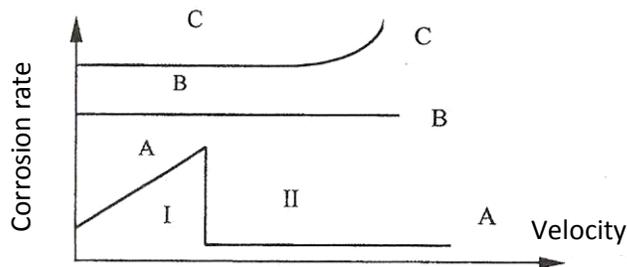
### *Effect of velocity*

The effect of velocity on corrosion rate is, like the effects of oxidizer additions, complex and depends on the characteristics of the metal and

environment to which it is exposed. The following figure shows typical observations when agitation or solution velocity is increased. For corrosion processes which are controlled by activation polarization, agitation and velocity have no effect on the corrosion rate as illustrated in curve B. If the corrosion process is under cathodic diffusion control, then agitation increases the corrosion rate as shown in curve A, section I. This effect generally occurs when an oxidizer is present in very small amounts, as is the case for dissolved oxygen in acids or water.

If the process is under diffusion control and the metal is readily passivated, then the behavior corresponding to curve A, section I and II, will be observed. That is, with increasing agitation, the metal will undergo an active – to – passive transition.

Some metals own their corrosion resistance in certain medium to the formation of massive bulk protective films on their surfaces. These films differ from the usual passivating films in that they are readily visible and much less tenacious. It is believed that both lead and steel are protected from attack in sulfuric acid by insoluble sulfate films. When materials such as these are exposed to extremely high corrosive velocities, mechanical damage or removal of these films can occur, resulting in accelerated attack as shown in curve C. This is called erosion corrosion.



C	B	A(I+II)	A(I)
-Pb in dilute H <sub>2</sub> SO <sub>4</sub>	-Fe in dilute HCl	-18Cr+8Ni in H <sub>2</sub> SO <sub>4</sub> +Fe <sup>+2</sup>	-Fe in O <sub>2</sub> +H <sub>2</sub> O
-Fe in con. H <sub>2</sub> SO <sub>4</sub>	-18Cr+8Ni in H <sub>2</sub> SO <sub>4</sub>	-Ti in Cu <sup>+2</sup> +HCl	-Cu in O <sub>2</sub> +H <sub>2</sub> O

### *Effect of temperature*

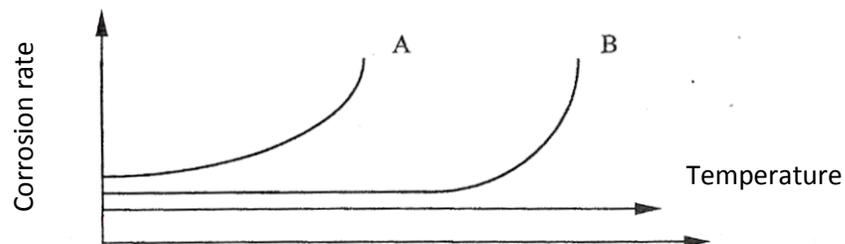
Temperature increases the rate of almost all chemical reactions. The following figure illustrates two common observations on the effect of temperature on the corrosion rates of metals. Curve A represents the behavior noted above, a very rapid or exponential rise in corrosion rate with increasing temperature. Behavior such as noted in curve B is also quite frequently observed. That is, an almost negligible temperature effect followed by a very rapid rise in corrosion rate at higher temperatures.

It is possible that curves such as B in many instances erroneously represent actual behavior. If the corrosion rate at low temperature is very low, and increases exponentially, linear plots will appear as curve B.

The relationship between corrosion rate and temperature can be seen through Arrhenius equation:

$$Rate = Ae^{\frac{E_a}{RT}}$$

Where A Arrhenius constant,  $E_a$  Activation energy,  $R$  gas constant and  $T$  temperature in Kelvin.



Curve A:

Fe in (HF), Ni in (HCl), SS in (H<sub>2</sub>SO<sub>4</sub>)

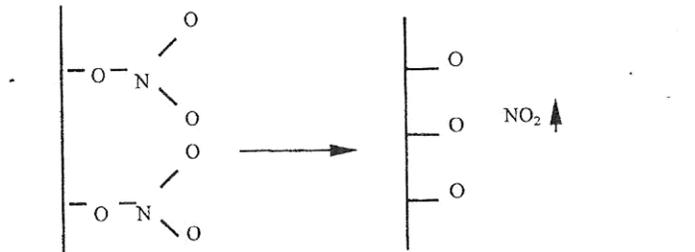
Curve B:

Ni in (NaOH), SS in (HNO<sub>3</sub>), Monel in (HF).

### ***Effect of anions and cations***

There are different behavior for anions and cations which presence in the environment:

$NO_3^-$ : this anion is oxidizer agent and can be adsorb on the surface to produce protective layer in static environment, but can be removed in dynamic environment.



$Cr^{3+}$ : this cation increases corrosion resistance of iron, where act as anode when it adsorb on the surface of iron which can act as cathode ( $E^{\circ}_{Cr}=-0.74V$ ,  $E^{\circ}_{Fe}=-0.44V$ ).

$Cu^{2+}$ : this cation decrease the corrosion resistance of iron because it is more noble than iron ( $E^{\circ}_{Cu}=+0.337V$ ).

## **Corrosion protection**

### ***1-Selection of materials***

When selecting materials, each component must be considered with respect to design, manufacture and its effect on the total geometry. However,

it is also important that the materials in adjacent components are compatible. With regard to corrosion, compatibility often means that detrimental galvanic elements must be avoided. Not only the main structural materials, but also insulation and other secondary materials must be taken into account to prevent galvanic corrosion.

In many cases it is possible to avoid other forms of corrosion by using a favourable combination of materials, e.g. to include a material that implies cathodic protection against uniform, selective, pitting, crevice or erosion corrosion on critical regions, even against stress corrosion cracking or corrosion fatigue. Not only do the grades of structural, load-bearing materials have to be specified, but also surface treatment and coatings.

The corrosion properties and other functional properties of materials depend on several external factors such as geometry, manufacture, surface conditions, environmental factors and mechanical load conditions. For each functional property, these factors have to be evaluated. The final materials selection is often a result of compromises between various properties and their dependence on external factors.

A proper selection of materials depends on sufficient knowledge on how the actual practical conditions affect each material candidate. To ensure that important aspects are not forgotten, check lists should be used, which should include risk of different forms of corrosion for each candidate, relevant conditions affecting each form of corrosion, possibilities of changing the corrosion properties of a certain material, possibilities for application of various protection methods, accessibility for maintenance, environmental conditions, loads and special requirements during various parts of the lifetime etc. Aspects related to other functional properties than the corrosion properties should of course be treated in similar ways.

The best tools for weighing the various aspects are quantitative expressions of properties and performance data valid under various conditions, such as corrosion rate and distribution, lifetime in corrosion fatigue, mechanical or electrochemical threshold values, compared with corresponding quantified requirements or service conditions, i.e. specified lifetime, actual stress intensity factors and functions, and corrosion potential.

The spectrum of different kinds of material data increases, but so do the number of possible material candidates. During planning of large and expensive structures and plants, the amount of relevant data can be increased by standardized or more or less tailor-made testing. However, in many cases, the materials have to be selected partly on the basis of qualitative information or stipulated characters representing corrosion properties.

The simplest way is to choose the material that has been used before for the same or some similar purpose. If the material selection plays a less important role, or if the risk and consequence of changing to a new material are uncertain, it may be preferable to stick to the same as before. However, as a general principle it is not acceptable. Nevertheless, previous selection for similar purposes is a part of the empirical bases that must be taken into account. Other factors are the policy of the company, market conditions, commercial relationships, standards, specifications and public requirements. Besides these aspects, and sometimes in conflict with some of them, the engineers have the responsibility to find the best technical-economic solution, which often must be based upon thorough knowledge about materials properties and a systematic analysis of the service conditions.

As a general guideline for materials selection primarily dictated by corrosion aspects, the reason for the corrosion resistance of the respective material candidates may be used. If the resistance is based upon:

1. Passivity, the alloy is suitable for oxidizing environments (only in the absence of species that promote localized corrosion).
2. Immunity, the alloy is suitable for reducing environments.

In several cases, non-metallic materials such as polymers, rubbers, ceramics, wood or concrete must also be taken into consideration. With respect to materials selection for screws, bolts, nuts, rivets or other small parts for use under possible galvanic corrosion conditions, it should be checked that they are a little more noble (have a little more positive corrosion potential in the actual environment) than the components they are binding together, or are in metallic contact with in any way. In addition, one should be particularly careful to avoid catastrophic deterioration forms such as hydrogen embrittlement, stress corrosion cracking and corrosion fatigue in such parts.

## ***2-Proper Design***

Design and materials selection are performed in connection with each other. In these processes both the individual components, the interactions between them and the relation to other structures and the surroundings have to be taken into account. The various phases of the life cycle of the construction, i.e. manufacturing, storing, transport, installation, operation and service, maintenance, and destruction should be considered.

The majority of the corrosion forms are affected more or less by the geometry: galvanic and thermogalvanic corrosion, crevice corrosion, erosion and cavitation corrosion, fretting corrosion, stress corrosion cracking and corrosion fatigue.

Some general guidelines are useful:

1. Design with sufficient corrosion allowance. Pipes, tanks, containers and other equipment are often made with a wall thickness twice the corrosion

depth expected during the desired lifetime. However, this must of course depend on load and maximum permissible stresses too.

2. Design such that the components that are most liable to corrosion are easy to replace. Special parts may be installed for “attracting” the corrosion.

3. For structures exposed to the atmosphere: the design should allow easy drainage with ample supply of air. Alternatively, the opposite: hinder air transport to cavities by complete sealing.

For components immersed in aqueous solutions there are similar extremes: efficient aeration should be secured (when this will cause passivation), or aeration should be prevented as far as possible.

4. Design in a way that makes drainage, inspection and cleaning easy. Use joints that do not cause corrosion problems, e.g. butt welds instead of overlap joints. However, in cases where the materials are protected by a paint or zinc coating before joining, sometimes it is beneficial to avoid welding. Alternatively, the welds can be post-treated (blast cleaned and coated, e.g. with paint, tape or thermal spray metal).

5. Avoid hot as well as cold spots. Heat exchangers and other equipment where heat transport occurs should be so designed that the surface temperature varies as little as possible. On superheated spots, increased (possibly thermogalvanic) corrosion will occur. For systems containing vapour, cold spots leading to local condensation and corrosion should be avoided.

6. Take the surroundings into account: make arrangements for minimizing the consequences of corrosion, e.g. where it may cause leakage. Make sure that separate systems do not impair the environment for each other. An example of this is if moisture containing copper ions (originating from

corrosion of a copper alloy pipe) can come in contact with aluminium components.

7. Avoid high corrosion risk on load-bearing parts or on critical places by shifting the attack to less critical places.

8. Aim at simple geometry, and avoid heterogeneity and sharp changes in the system. Heterogeneity comprises different metals, uneven temperature and stress distribution, uneven dimensions etc. Abrupt dimension changes are unfortunate for stress distribution, temperature distribution, flow conditions, and possibly for the ease of cleaning. Sharp edges and irregularities on the surface impair the basis for painting, electrolytic plating and hot dipping.

Welds may contribute to several such problems. Crevices may cause harm in more than one sense, for instance on parts that are going to be pickled, since pickling acid may be entrapped and cause corrosion. Complex geometry and narrow gaps impede surface treatment such as blast cleaning, painting and thermal spraying, increase the cost, and make it more difficult to keep the structure clean and dry.

9. Design for flow velocities that are compatible with the selected materials.

10. Adjust pressure on gaskets (depending on gasket material) to avoid penetration of liquid into crevices.

### ***3-Inhibitors***

The use of chemical inhibitors to decrease the rate of corrosion processes is quite varied. In the oil extraction and processing industries, inhibitors have always been considered to be the first line of defense against corrosion. A great number of scientific studies have been devoted to the

subject of corrosion inhibitors. However, most of what is known has grown from trial and error experiments, both in the laboratories and in the field.

Rules, equations, and theories to guide inhibitor development or use are very limited. By definition, a corrosion inhibitor is a chemical substance that, when added in small concentration to an environment, effectively decreases the corrosion rate. The efficiency of an inhibitor can be expressed by a measure of this improvement:

$$P\% = \left(1 - \frac{R}{R_o}\right) \times 100$$

$$\text{or} = \left(1 - \frac{i}{i_o}\right) \times 100$$

In general, the efficiency of an inhibitor increases with an increase in inhibitor concentration (e.g., a typically good inhibitor would give 95% inhibition at a concentration of 0.008% and 90% at a concentration of 0.004%). A synergism, or cooperation, is often present between different inhibitors and the environment being controlled, and mixtures are the usual choice in commercial formulations. The scientific and technical corrosion literature has descriptions and lists of numerous chemical compounds that exhibit inhibitive properties. Of these, only very few are actually used in practice. This is partly because the desirable properties of an inhibitor usually extend beyond those simply related to metal protection. Considerations of cost, toxicity, availability, and environmental friendliness are of considerable importance.

#### - *Classification of Inhibitors*

Inhibitors are chemicals that react with a metallic surface, or the environment this surface is exposed to, giving the surface a certain level of

protection. Inhibitors often work by adsorbing themselves on the metallic surface, protecting the metallic surface by forming a film. Inhibitors are normally distributed from a solution or dispersion. Some are included in a protective coating formulation. Inhibitors slow corrosion processes by

- \_ Increasing the anodic or cathodic polarization behavior (Tafel slopes)
- \_ Reducing the movement or diffusion of ions to the metallic surface
- \_ Increasing the electrical resistance of the metallic surface

Inhibitors have been classified differently by various authors. Some authors prefer to group inhibitors by their chemical functionality, as follows:

### **1- Inorganic inhibitors**

Usually crystalline salts such as sodium chromate, phosphate, or molybdate. Only the negative anions of these compounds are involved in reducing metal corrosion. When zinc is used instead of sodium, the zinc cation can add some beneficial effect. These zinc-added compounds are called mixed-charge inhibitors.

### **2- Organic anionic**

Sodium sulfonates, phosphonates, or mercaptobenzotriazole (MBT) are used commonly in cooling waters and antifreeze solutions.

### **3- Organic cationic**

In their concentrated forms, these are either liquids or waxlike solids. Their active portions are generally large aliphatic or aromatic compounds with positively charged amine groups.

However, by far the most popular organization scheme consists of regrouping corrosion inhibitors in a functionality scheme as follows.

#### *1- Passivating (anodic)*

Passivating inhibitors cause a large anodic shift of the corrosion potential, forcing the metallic surface into the passivation range. There are two types of passivating inhibitors: oxidizing anions, such as chromate, nitrite, and nitrate, that can passivate steel in the absence of oxygen and the nonoxidizing ions, such as phosphate, tungstate, and molybdate, that require the presence of oxygen to passivate steel.

These inhibitors are the most effective and consequently the most widely used. Chromate-based inhibitors are the least-expensive inhibitors and were used until recently in a variety of application (e.g., recirculation-cooling systems of internal combustion engines, rectifiers, refrigeration units, and cooling towers). Sodium chromate, typically in concentrations of 0.04 to 0.1%, was used for these applications.

At higher temperatures or in fresh water with chloride concentrations above 10 ppm higher concentrations are required. If necessary, sodium hydroxide is added to adjust the pH to a range of 7.5 to 9.5. If the concentration of chromate falls below a concentration of 0.016%, corrosion will be accelerated. Therefore, it is essential that periodic colorimetric analysis be conducted to prevent this from occurring. In general, passivation inhibitors can actually cause pitting and accelerate corrosion when concentrations fall below minimum limits. For this reason it is essential that monitoring of the inhibitor concentration be performed.

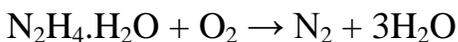
## *2- Cathodic*

Cathodic inhibitors either slow the cathodic reaction itself or selectively precipitate on cathodic areas to increase the surface impedance and limit the diffusion of reducible species to these areas. Cathodic inhibitors can provide inhibition by three different mechanisms:

(1) as cathodic poisons, (2) as cathodic precipitates, and (3) as oxygen scavengers. Some cathodic inhibitors, such as compounds of arsenic and antimony, work by making the recombination and discharge of hydrogen more difficult.

Other cathodic inhibitors, ions such as calcium, zinc, or magnesium, may be precipitated as oxides to form a protective layer on the metal.

Oxygen scavengers help to inhibit corrosion by preventing the cathodic depolarization caused by oxygen. The most commonly used oxygen scavenger at ambient temperature is probably sodium sulfite ( $\text{Na}_2\text{SO}_3$ ).



### 3- Organic

Both anodic and cathodic effects are sometimes observed in the presence of organic inhibitors, but as a general rule, organic inhibitors affect the entire surface of a corroding metal when present in sufficient concentration. Organic inhibitors, usually designated as film-forming, protect the metal by forming a hydrophobic film on the metal surface.

Their effectiveness depends on the chemical composition, their molecular structure, and their affinities for the metal surface. Because film formation is an adsorption process, the temperature and pressure in the system are important factors. Organic inhibitors will be adsorbed according to the ionic charge of the inhibitor and the charge on the surface.

Cationic inhibitors, such as amines, or anionic inhibitors, such as sulfonates, will be adsorbed preferentially depending on whether the metal is charged negatively or positively. The strength of the adsorption bond is the dominant factor for soluble organic inhibitors. These materials build up a protective film of adsorbed molecules on the metal surface, which provides a barrier to the dissolution of the metal in the electrolyte. Because the metal surface covered is proportional to the inhibitor concentration, the concentration of the inhibitor in the medium is critical. For any specific inhibitor in any given medium there is an optimal concentration. For example, a concentration of 0.05% sodium benzoate or 0.2% sodium cinnamate is effective in water with a pH of 7.5 and containing either 17 ppm sodium chloride or 0.5% by weight of ethyl octanol. The corrosion due to ethylene glycol cooling water systems can be controlled by the use of ethanalamine as an inhibitor.

$$Q_{inh.} = \frac{V_{fluid}}{1 \times 10^6} \times C_{inh.(ppm)}$$

#### 4- Precipitation inhibitors

Precipitation-inducing inhibitors are film-forming compounds that have a general action over the metal surface, blocking both anodic and cathodic sites indirectly. Precipitation inhibitors are compounds that cause the formation of precipitates on the surface of the metal, thereby providing a protective film. Hard water that is high in calcium and magnesium is less corrosive than soft water because of the tendency of the salts in the hard water to precipitate on the surface of the metal and form a protective film.

The most common inhibitors of this category are the silicates and the phosphates. Sodium silicate, for example, is used in many domestic water softeners to prevent the occurrence of rust water. In aerated hot water

systems, sodium silicate protects steel, copper, and brass. However, protection is not always reliable and depends heavily on pH and a saturation index that depends on water composition and temperature.

Phosphates also require oxygen for effective inhibition. Silicates and phosphates do not afford the degree of protection provided by chromates and nitrites; however, they are very useful in situations where nontoxic additives are required.

#### *5- Volatile corrosion inhibitors*

Volatile corrosion inhibitors (VCIs), also called vapor phase inhibitors (VPIs), are compounds transported in a closed environment to the site of corrosion by volatilization from a source. In boilers, volatile basic compounds, such as morpholine or hydrazine, are transported with steam to prevent corrosion in condenser tubes by neutralizing acidic carbon dioxide or by shifting surface pH toward less acidic and corrosive values. In closed vapor spaces, such as shipping containers, volatile solids such as salts of dicyclohexylamine, cyclohexylamine, and hexamethylene-amine are used.

On contact with the metal surface, the vapor of these salts condenses and is hydrolyzed by any moisture to liberate protective ions. It is desirable, for an efficient VCI, to provide inhibition rapidly and to last for long periods. Both qualities depend on the volatility of these compounds, fast action wanting high volatility, whereas enduring protection requires low volatility.

#### ***- Corrosion Inhibition Mechanism***

The majority of inhibitor applications for aqueous, or partly aqueous, systems are concerned with four main types of environment:

1. Aqueous solutions of acids as used in metal-cleaning processes such as pickling for the removal of rust or mill scale during the production and fabrication of metals or in the postservice cleaning of metal surfaces.
2. Natural waters, supply waters, and industrial cooling waters in the near-neutral pH range (5 to 9)
3. Primary and secondary production of oil and subsequent refining and transport processes.
4. Atmospheric or gaseous corrosion in confined environments, during transport, storage, or any other confined operation.

The following sections describe corrosion mechanisms in terms of these four main environments.

#### 1- Inhibitors for acid solutions

The corrosion of metals in acid solutions can be inhibited by a wide range of substances, such as halide ions, carbon monoxide, and many organic compounds, particularly those containing elements of Groups V and VI of the Periodic Table (i.e., nitrogen, phosphorus, arsenic, oxygen, sulfur, and selenium). Organic compounds containing multiple bonds, especially triple bonds, are effective inhibitors. The primary step in the action of inhibitors in acid solutions is generally agreed to be adsorption onto the metal surface, which is usually oxide-free in acid solutions. The adsorbed inhibitor then acts to retard the cathodic and/or anodic electrochemical corrosion processes.

Inhibitors of corrosion in acid solution can interact with metals and affect the corrosion reaction in a number of ways, some of which may occur simultaneously. It is often not possible to assign a single general mechanism of action to an inhibitor because the mechanism may change with

experimental conditions. Thus, the predominant mechanism of action of an inhibitor may vary with factors such as its concentration, the pH of the acid, the nature of the anion of the acid, the presence of other species in the solution, the extent of reaction to form secondary inhibitors, and the nature of the metal. The mechanism of action of inhibitors with the same functional group may additionally vary with factors such as the effect of the molecular structure on the electron density of the functional group and the size of the hydrocarbon portion of the molecule.

## 2- Inhibitors in near-neutral solutions

Corrosion of metals in neutral solutions differs from that in acid solutions in two important respects. In air-saturated solutions, the main cathodic reaction in neutral solutions is the reduction of dissolved oxygen, whereas in acid solution it is hydrogen evolution. Corroding metal surfaces in acid solution are oxide-free, whereas in neutral solutions metal surfaces are covered with films of oxides, hydroxides, or salts, owing to the reduced solubility of these species. Because of these differences, substances that inhibit corrosion in acid solution by adsorption on oxide-free surfaces do not generally inhibit corrosion in neutral solution.

Typical inhibitors for near-neutral solutions are the anions of weak acids, some of the most important in practice being chromate, nitrite, benzoate, silicate, phosphate, and borate. Passivating oxide films on metals offer high resistance to the diffusion of metal ions, and the anodic reaction of metal dissolution is inhibited. These inhibitive anions are often referred to as anodic inhibitors, and they are more generally used than cathodic inhibitors to inhibit the corrosion of iron, zinc, aluminum, copper, and their alloys in near-neutral solutions. The action of inhibitive anions on the

corrosion of metals in near-neutral solution involves the following important functions:

1. Reduction of the dissolution rate of the passivating oxide film
2. Repair of the oxide film by promotion of the reformation of oxide
3. Repair of the oxide film by plugging pores with insoluble compounds
4. Prevention of the adsorption of aggressive anions

### 3- Inhibitors for oil and gas systems

Even in early days, oil producers applied numerous chemical compounds, sometimes with success, to minimize corrosion damage in the oil wells themselves and in surface handling equipment. Once amines and imidazolines came into use, corrosion inhibition in oil wells became dramatically more effective. Modern inhibitors are applied in the field, continuously or by periodic batch, at concentrations of 15 to 50 ppm, based on total liquid production. A much wider variety of inhibitor chemistry is available today for combating oil-field corrosion than existed only a decade ago. In recent years, organic molecules containing sulfur, phosphorus, and nitrogen in various combinations have been developed. These inhibitor types have extended the performance of oil-field inhibitors, particularly in the directions of being tolerant of oxygen contamination and of controlling corrosion associated with high CO<sub>2</sub>, low H<sub>2</sub>S conditions.

Most of the inhibitors currently used in producing wells are organic nitrogenous compounds. The basic types have long-chain hydrocarbons (usually C<sub>18</sub>) as a part of the structure. Most inhibitors in successful use today are either based on the long-chain aliphatic diamine, or on long carbon chain imidazolines. Various modifications of these structures have been made to change the physical properties of the material (e.g., ethylene oxide is commonly reacted with these compounds in various molecular

percentages to give polyoxy-ethylene derivatives that have varying degrees of brine dispersibility). Many carboxylic acids are used to make salts of these amines or imidazolines.

Inhibitors in general petroleum production can be classified as follows:

- \_ Amides/imidazolines
- \_ Salts of nitrogenous molecules with carboxylic acids
- \_ Nitrogen quaternaries
- \_ Polyoxyalkylated amines, amides, and imidazolines
- \_ Nitrogen heterocyclics and compounds containing P, S, O

#### 4- Atmospheric and gaseous corrosion

VCI's represent a very economical and powerful tool in combating the atmospheric or gaseous corrosion damage done to metals and alloys. Volatile corrosion inhibition is based on conditioning of the environment with trace amounts of inhibitive material to achieve a protective effect. A VCI compound, in addition to being volatile, is required to promote electrochemical effects such as change of the potential in the diffuse part of the double layer that controls the migration of components of the electrode reactions.

The first condition for good efficiency of a vapor phase inhibitor is its capability to reach the metallic surface to be protected. The second is that the rate of transfer of the molecule should not be too slow to prevent an initial attack of the metal surface by the aggressive environment before the inhibitor can act. These two conditions are related partly to the vapor pressure of the inhibitor, partly to the distance between the source(s) of the

inhibitor and the metal surfaces, and partly to the accessibility of the surfaces.

#### **4- Electrical protection**

##### ***- Cathodic protection***

Cathodic protection (CP) has been known for about 170 years. Primarily it has been used for protection of ordinary structural steel in soil and seawater, more seldom (and under special conditions) for steel exposed to fresh water. Other materials can also be protected by CP, for instance to prevent localized corrosion on stainless steel and aluminium. CP has in most cases been applied in combination with a coating, with the intention to protect the steel on “holidays” and damaged areas of the coating. In recent decades the application of this technology has increased considerably in connection with the expanding offshore oil and gas exploration and production.

It is the dominating protection method for the large submerged parts of fixed oil installations, most often the only one for the parts freely exposed to seawater.

##### ***- Principle***

The main principle of CP is to impress an external current on the material, which forces the electrode potential down to the immune region, or, for protection against localized corrosion, below a protection potential. In other words, the material is made the cathode in an electrochemical cell; it is polarized cathodically as illustrated by potential-log current curves. The external current  $I_e$  is the difference between the cathodic and the anodic

current at the actual potential  $E_c$ . At this potential, the anodic current on the protected material is very low, i.e. the external current is nearly equal to the cathodic current.

The external current can be produced in two different ways:

- a) By means of a less noble material in the form of sacrificial anodes, which are connected by metallic conductors to the structure to be protected.
- b) By means of an external current source, usually a rectifier. A reference electrode may be used to control the rectifier potentiostatically.

### ***- Protection Criteria and Specifications***

In most cases it is appropriate to use a potential criterion for CP. The main criterion is  $E_c < E_p$ , where  $E_p$  is a protection potential defined mainly upon an empirical basis. For steel in seawater, the following protection potential has usually been recommended, referred to the various reference electrodes:

<i>Cu/CuSO<sub>4</sub></i>	<i>Ag/AgCl/seawater</i>	<i>Zn</i>	<i>SCE</i>	<i>SHE</i>
-850 mV	-800 mV	-250 mV	-780 mV	-530 mV

This potential is 90 mV above the equilibrium potential of the reaction  $Fe^{2+} + 2e = Fe$  at an activity of  $Fe^{2+} = 10^{-6}$ . The stated value of the protection potential corresponds to the equilibrium potential at a ferrous ion activity of  $10^{-3}$ .

### ***- Cathodic Protection with Sacrificial Anodes***

The majority of offshore installations, particularly in aggressive environments such as in the North Sea, are protected with sacrificial anodes. On submerged parts of fixed platforms, this is in most cases the only

protection system. A few oil companies have used a combination of a paint coating system and sacrificial anodes, while a combination of thermally sprayed aluminium and sacrificial anodes have been used in special cases. Combinations of coatings and CP and/or a combination of sacrificial anodes and impressed current may be of particular interest for the reduction of weight and drag forces from the anodes on structures in deep water.

Floating platforms are generally protected by CP (sacrificial anodes or impressed current) combined with a high-quality paint system. Pipelines with an organic coating and an external concrete coating are also protected by sacrificial anodes. For bare steel on offshore structures in seawater, the sacrificial anodes are commonly made of special aluminium alloys because these give the highest current output for a certain anode weight as well as the lowest cost.

Zn anodes are usually applied on coated and buried pipelines offshore, where the risk for passivation of Al anodes is higher due to a lower CD. When sacrificial anodes (usually Zn or Al) are used on ship hulls they are combined with a paint system. The anodes are mounted close to each other on the area around the propeller, partly because the propeller “steals” some of the current and partly because of turbulence leading to higher demand of cathodic current density. Zn and Al anodes are also used in ballast tanks on tankers and bulk carriers.

For some other applications, such as on steel structures in soil, and in hot water tanks for fresh water, magnesium anodes are used to a higher extent. In these cases Mg anodes have a great benefit in higher driving voltage than the Al and Zn anodes.

In high-resistivity environments, a combination of CP and coating is particularly beneficial with the aim to reduce the total current and thereby

the potential drop near the anodes, and thus to obtain a better distribution of the current to the spots where it is needed.

A sacrificial anode system can be designed in the following way. The exact description of the procedure is a little different in different sources, but the principles are the same:

1. The surface area  $A_c$  of the structure is calculated in a reasonably conservative way. Areas with different current density demand must be calculated separately.
2. Design values of CD ( $I_c$ ) on the steel surface are chosen.
3. The total current demand,  $I_t = I_c \cdot A_c$ , is calculated. If the steel is coated, the current must be multiplied by a coating breakdown factor  $f_b$ .
4. Material, shape and size of the anodes are selected, and the anode resistance  $R_a$  is calculated by use of the appropriate formula.
5. The current output from each anode is given by

$$I_a = \Delta E_a / R_a$$

where  $E_a$  is the potential difference that is available for overcoming  $R_a$ .

6. The number of anodes is calculated:

$$n \geq I_t / I_a$$

It should be noticed that both the current demand it and the output from each anode  $I_a$  is reduced during the service time. The number of anodes should therefore be calculated both for the initial and for the final stage. The largest of the calculated n-values is chosen.

7. The total weight of anodes necessary to protect the structure during the specified lifetime  $t^*$  is calculated:

$$G_t = I_m \times t / C \times u$$

where  $I_m$  is the average (mean) current demand =  $\Sigma i_m \times A_c$ ,  $C$  is the anode capacity and  $u$  the utilization factor. Then it is checked that

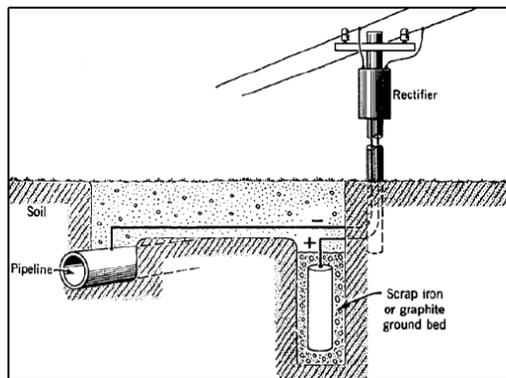
$$n \geq G_t / G_a$$

where  $G_a$  is the weight of each anode.

$E_a$ ,  $I_a$ ,  $C$ ,  $u$  and other anode data are available from anode suppliers.

### ***- Cathodic Protection with Impressed Current***

When such a system is used on fixed offshore platforms it may be preferable to combine it with sacrificial anodes (hybrid system). Then, the sacrificial anodes can protect the structure before the impressed current installation is ready for use, and also contribute to a better current distribution. The largest benefits of impressed current compared with sacrificial anodes are lower anode weight and lower drag forces from the sea. Also, relatively few anodes are necessary. Theoretically, it is a more economic solution than sacrificial anodes, but practical experience with cases of serious mechanical damage of the CP system has led to fewer applications of impressed current systems.



**- Electrolyte Resistance, Potential Variation and Current Distribution in CP Systems and Galvanic Elements**

The simplest possible geometry of a galvanic element is characterized by plane parallel and equally large electrodes (anode and cathode) and between the electrodes an electrolyte volume with a cross-section identical with each electrode area, and consequently (provided a homogeneous electrolyte) parallel current paths. For this model, there is a potential drop in the electrolyte over the length  $l$  from the anode to the cathode given by

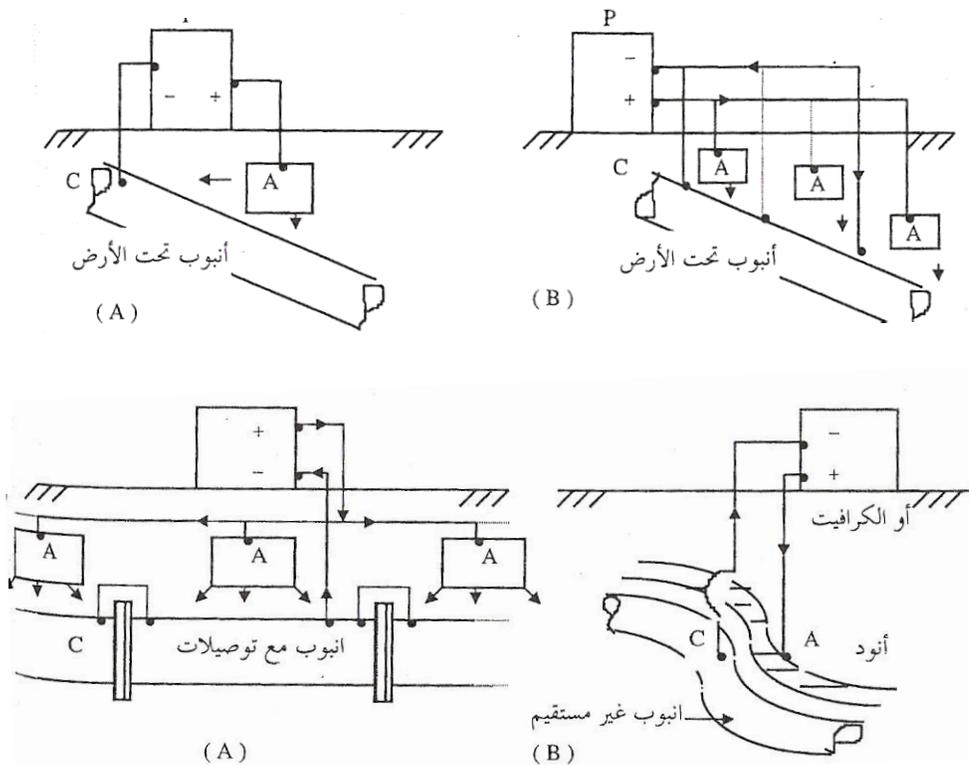
$$\Delta E = I R = i A \rho \ l/A = i \rho^* l$$

and we can call it a linear model.

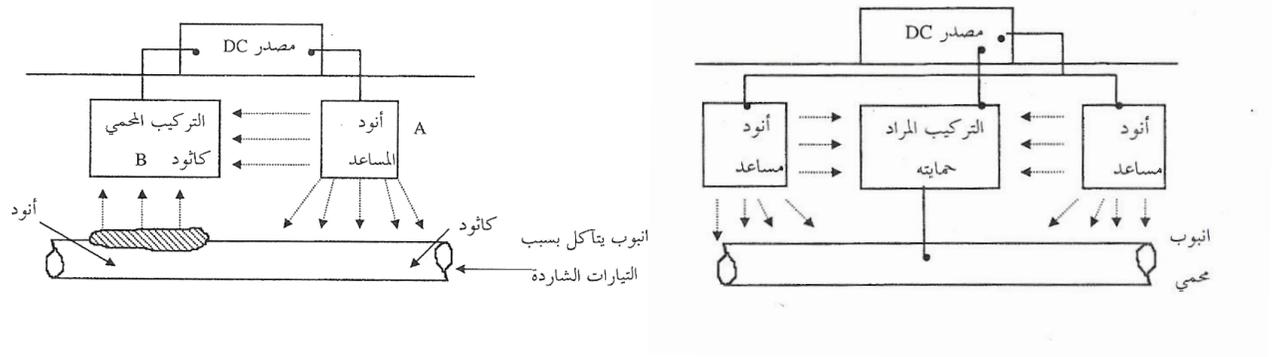
$$E_{CP} = i_{CP}(R_C + R_A + R_E)$$

Other simple models are the cylindrical and the spherical model, where the two electrodes are concentric shells with radii  $r_i$  and  $r_o$ , respectively, and the current paths are radial.

There are many rules can be follow in the application of cathodic protection as shown in the following figures:



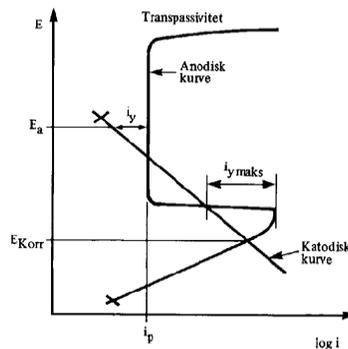
### Stray current



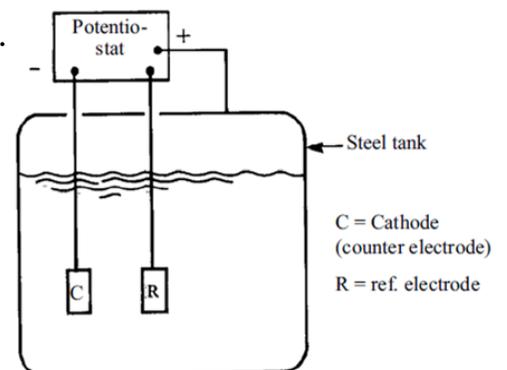
### Anodic Protection

Anodic protection can be applied on materials with a well-defined and reliable passive region and low passive current density, i.e. with an anodic overvoltage curve like that shown in following figure. The material is polarized in the anodic direction so that the potential is shifted to the passive region. As indicated in the figure, the current density necessary to hold the potential  $E_a$  at a suitable value is low, and this makes the method economic in use. However, the initial current density  $i_{max}$  may be relatively high.

$$E_{Applied} = \frac{E_{PP} + E_{TP}}{2}$$



Following figure shows in principle the arrangement for internal protection of a steel tank by means of a potentiostat.



Anodic protection is used on objects such as steel tanks for storing and transport of sulphuric acid, apparatus made of stainless steels and titanium for treatment of various acids and salt solutions, and for aluminium exposed to water at high temperature. The method cannot be used in aggressive liquids that may cause localized corrosion or high passive current density. It may be used on 18/8 CrNi stainless steel exposed to 30% H<sub>2</sub>SO<sub>4</sub> + 1% NaCl and on titanium exposed to hydrochloric acid solutions.

Pitting is avoided, in the former case because the sulphate ions counteract the chloride, in the latter case because the pitting potentials of titanium in the actual solutions are very high.

Anodic protection might be utilized much more than it has been so far, but the method must not be used under unfavourable conditions, because the anodic polarization may cause a strong increase of the corrosion rate. If there is any doubt, laboratory experiments may clarify if anodic protection can be recommended.

## ***5-Coatings***

Through the application of coatings, corrosion is prevented by one of the following three main mechanisms or by combination of two of them:

- i) Barrier effect, where any contact between the corrosive medium and the metallic material is prevented.
- ii) Cathodic protection, where the coating material acts as a sacrificial anode.
- iii) Inhibition/passivation, including cases of anodic protection.

In the following sections, a survey of different types of coating is given, which includes properties, mode of action, fields of application, and coating methods. Without regard to the type of coating and the application

method, a proper pretreatment of the material to be protected is necessary for obtaining a good result.

### ***Metallic Coatings***

In most cases of corrosion protection by metallic coatings, the purpose is to protect unalloyed or low-alloy steel, but there also exist many cases of other metals to be protected this way. Metallic coatings can be divided in two groups, the cathodic coatings, which are more noble than the substrate, and the anodic ones, which are less noble than the substrate, i.e. the coatings that have, respectively, a higher and a lower corrosion potential than the substrate in the environment in question.

The *cathodic coatings* will most often act by the barrier effect only, but for some combinations of substrate and environment the substrate can also be anodically protected (on uncovered spots). The *anodic coatings* will in addition to the barrier effect provide cathodic protection of possible “holidays” , i.e. spots or parts of the surface where the coating is imperfect and the substrate is exposed to the corrosive environment. The normal major difference between a cathodic and an anodic coating is just the behaviour at such a defect.

In relation to steel, Ag, Ni, Cr and Pb are cathodic, while Zn and Cd are anodic in most environments. The polarity of Sn and Al referred to steel varies from one environment to another.

*Silver* is used as a coating material for decoration purposes; furthermore its chemical and electrical properties are utilized, respectively, in various equipment and environments in the process industry and in electric contacts and other small components in electrical and electronic equipment. Silver coatings are commonly applied by electrolytic plating.

A coating of copper or nickel is often used under the silver top coat. Silver may be attacked by sulphides in industrial atmospheres. To prevent attack, sometimes a thin layer of rhodium is used on top of the silver coating; alternatively, a passivating chemical treatment is carried out.

*Nickel* has often been used for preventing corrosion and for providing a nice surface on steel parts in contact with ordinary atmosphere, e.g. bicycle parts, car parts and fittings. In order to make the surface brighter and more corrosion resistant the nickel plate is covered by a thin coating of chromium. Depending on the service conditions and the type of nickel and chromium coating, the recommended thickness of nickel can vary from 5 to 40  $\mu\text{m}$  and of chromium from 0.3 to 0.8  $\mu\text{m}$ . The chromium coating has a large number of micropores or microcracks, which is advantageous because they make the corrosion of the underlying nickel well distributed and shallow. The chromium layer is usually deposited on top of a thin layer of bright nickel, which is anodic in relation to a thicker basic layer of (semi) matt nickel.

Because of its less noble nature, the bright nickel layer gives a certain cathodic protection effect on the basic layer in existing pores. A basic layer of copper may be used on iron and steel substrates, which allows a thinner nickel coating. Nickel-chromium coatings can also be used on zinc (with a basic layer of copper), on copper alloys and aluminium alloys.

For industrial use, nickel coatings are applied without chromium on top, and the coatings are most often thicker, usually 25-250  $\mu\text{m}$ , and up to 500  $\mu\text{m}$  for some applications. Such coatings are most suitable for environments that tend to cause general corrosion with reaction products of low solubility (environments without chlorides). However, it is also stated

that nickel performs well in seawater provided that the flow rate is high. Furthermore, the experience with nickel in various alkalis, neutral and alkaline salts and organic chemicals is good.

Electrochemical deposition (electroplating) has traditionally been, and is still, the dominating technique for application of nickel coatings. In recent years, the number of applications of chemical (electroless) deposits of nickel has been growing (parts in pumps, valves, compressors, storage vessels for chemicals etc). Nickel coatings can increase the resistance to corrosion fatigue, but stresses set up by the coating may reduce the pure mechanical fatigue strength of the base material.

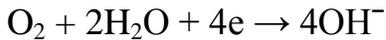
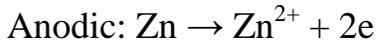
The effect can be counteracted by compression stresses in the coating, which can be obtained with certain electrolytic baths, or by applying a soft basic coating (tin, lead), which can prevent cracks in the coating propagating into the base material.

Thick or so-called hard chromium coatings are used directly on steel, cast iron and light alloys to improve resistance to wear and corrosion in hydraulic cylinders, pump shafts, bearings, dies etc. Thermodynamically, chromium is less noble than iron, but under atmospheric and many other conditions it is practically more noble due to the strong tendency to passivation.

*Lead* is particularly suitable in coatings exposed to dilute sulphuric acid and industrial atmospheres.

*Tin* shows rather complicated corrosion properties in contact with steel. In the atmosphere and in solutions of natural inorganic salts, Sn is cathodic in relation to Fe. In contact with fruit juice, meat, milk and alkaline solutions, tin is anodic. Tin plating is most often carried out by electrochemical deposition, but hot dipping is also common.

*Zinc.* The boundaries of the passivity region shown by solid lines are valid for water without CO<sub>2</sub>. For pH < 8-9, the following reactions occur:



The equilibrium potentials of the three reactions as functions of pH are drawn in the diagram. For pH values between 8.5 and 11, zinc is passivated by formation of Zn(OH)<sub>2</sub>. When CO<sub>2</sub> is dissolved in the corrosive medium the passive region is enlarged so that it reaches from pH = 6 to pH = 11. The reason for this is the formation of a protective film of alkaline zinc carbonate.

Zinc is easy to apply electrochemically, by hot dipping, and by thermal spraying. A fourth method is sherardizing. Electrochemically applied coatings are relatively thin, usually up to 25 μm, and they are in most cases post-treated with a converting process, such as chromating, which gives a yellow, blue, drab or colourless appearance. Hot-dipped zinc coatings are often 80-100 μm thick, and a typical thickness range for thermal spray Zn is 100-200 μm, and these two methods can therefore provide more long-term protection under suitable conditions.

*Aluminium.* As a coating material it is applied in thermal spraying (metal spraying) both on land-based and on offshore steel structures. Hot dipping is a more sensitive process with aluminium than with zinc as coating material, and it has not obtained the same widespread application for Al as it has for Zn. Hot-dipped coatings produced of mixtures of aluminium and zinc have shown good all-round properties for atmospheric exposure. Aluminium can also be plated by electrochemical as well as chemical deposition. Cladding

of surfaces can be carried out by rolling, extrusion, drawing, and explosive bonding.

In hard chloride-free water, Al corrodes too slowly to be able to protect the steel in coating defects. Conversely, in alkaline solutions aluminium corrodes too fast, which results in too short a lifetime of the coating. Aluminium normally corrodes more slowly than zinc in marine atmospheres and seawater.

*Cadmium* has been a very useful coating material, but because of its toxic nature the numbers of applications have been reduced during recent decades.

### **- Coating Methods**

A few characteristic features of three of the methods for applying metal coatings, namely electrolytic plating, hot dipping and thermal spraying, will be summarized here.

- *Electrolytic plating.* Compared with other coating methods, electrolytic deposition is favoured by low process temperatures. Hence, any heat effect, which might cause changes in structure, shape and mechanical properties of the substrate, is avoided. As for other methods, both local and overall geometry of the surface to be coated must be carefully considered as part of the design work.

Cavities, where air or liquid may be enclosed, cannot be accepted, and sharp corners should be avoided. Since the coating usually is thin (5-40  $\mu$  m), factors such as roughness and porosity in the substrate may cause problems that do not exist for the methods where thicker coatings are common.

For electrolytic deposition of zinc it is easier to control the coating thickness than it is for hot dipping and thermal spraying. Any brittle alloy, like the Zn-Fe layer that is typical in hot-dip galvanized coatings, does not exist in electroplated Zn coatings, i.e. the latter is more ductile. But the lifetime of zinc coatings is nearly proportional to the thickness, independent of coating method, and this limits the numbers of applications of electroplated Zn.

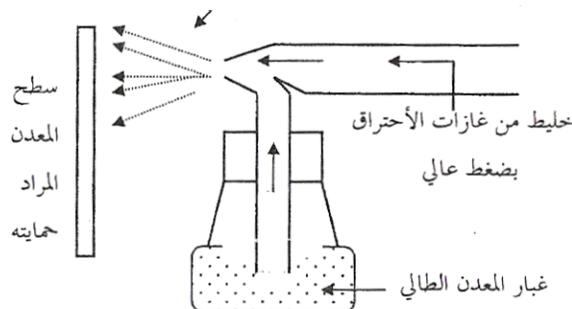
- *Hot dipping.* Zinc, tin and tin/lead coatings are commonly applied by hot dipping, i.e. dipping of the object to be coated in molten coating metal. Aluminizing by this method is less widespread, because Al makes the process more difficult to operate. Hot-dip galvanizing is the most economical method in cases where a relatively thick Zn coating (up to 100-200  $\mu$  m) is needed or desirable on components that can be placed in a bath without much difficulty. A common size limit is 12-13 m in length and 1-1.5 m in width, but baths that can take structures of dimensions up to 18 m  $\times$  2 m  $\times$  5 m exist.

The normal temperature of the galvanizing bath is 445-465°C. For thin uniform coatings, particularly on threaded components, a higher temperature is used (up to 560°C). At these temperature levels an alloy layer of Fe and Zn is formed, which constitutes a proportion of the coating thickness that depends on the steel type. Addition of Si to the steel affects the whole structure of the coating to a great extent. It is also used to regulate the coating thickness. The Fe-Zn alloy is hard and brittle. In galvanizing thin sheets a method is used that gives an alloy layer thickness of only a few

micrometres, and the sheets can therefore undergo metal-forming processes after galvanizing.

With respect to requirements on design, effects on mechanical and mechanical- technological properties (e.g. toughness, fatigue strength, weldability) and painting of zinc coatings, the zinc coating industry can give adequate information.

- *Thermal spraying*. The principles of thermal spray methods are shown in following figure. Flame and arc spraying are most common for prevention of low-temperature corrosion. Coated test samples have been studied after long-term exposure. Most metals can be sprayed. For corrosion protection of steel in waters and the atmosphere, aluminium and zinc are of particular importance. These coatings are usually from 100 to 300  $\mu$  m thick. Other materials such as stainless steel are also sprayed with good results and have important application, e.g. on machine parts and on cylinders in the pulp and paper industry. For these purposes the coatings are considerably thicker, e.g. up to a few millimetres. The special advantages of thermal spraying compared with other coating methods are just that thicker coatings can be applied, and particularly that the spraying equipment is portable, so that the coating work can be carried out almost anywhere. For large and fixed structures that cannot be hot-dip galvanized, thermal spraying is often the only alternative to painting.



Thermal spray aluminium and zinc coatings with a paint system on top provide first class corrosion protection with very long lifetime under most natural conditions, and have been extensively used on steel structures, e.g. road bridges.

In addition to the methods just described, several other principles for applying metal coatings exist, such as cladding (e.g. application by rolling nickel or stainless steel on carbon steel, or pure aluminium on a strong but less corrosion-resistant aluminium alloy), spot welding, overlay welding, chemical deposition, diffusion coating (performed at high temperature), and advanced methods such as physical and chemical vapour deposition (PVD and CVD), ion plating, and laser treatment.

### ***Other Inorganic Coatings***

Coatings in this group prevent corrosion by their barrier effect. The group comprises, among others, various types of enamel and glass linings. The coating material, which must have a suitable thermal expansion coefficient, is applied in the form of a powder (after pickling or other cleaning of the base material) and heated in a furnace until the lining material becomes soft and is bound to the metal surface.

High resistance to numerous chemicals and other environments can be obtained by variation of the composition of the coating material. The linings are brittle and can tolerate very little deformation, and some of them are sensitive to thermal shock.

Coatings of ordinary mortar (from Portland cement) have nearly the same thermal expansion coefficient as steel, and they are cheap and easy to repair. They can be applied with a thickness in the range 0.5-2.5 cm and more to protect pipelines and tanks, internally or externally. Thicker

coatings are often reinforced with a net. On internal cylindrical surfaces the coatings can be applied by centrifugal casting, or by spraying and manual finishing. Imperfections and damaged parts in the coating may cause concentrated attacks, particularly if there is a galvanic contact with more noble materials than steel, which can be the case in pipe systems including valves, pumps etc. The problem is avoided if the coating is combined with cathodic protection.

- *Ceramic coatings* of oxides, nitrides, borides etc. can be applied by thermal spraying. Some of the ceramic materials can be sprayed by the classical flame spraying method, while others must be plasma sprayed because the melting points are too high for the former method. Ceramic coatings are particularly used to prevent high-temperature corrosion and wear, and to provide thermal barriers (thermal insulation). Important alternatives in many cases are ceramic-metallic coatings that most often are composed of hard carbide particles bound together by a metallic material. These materials are also called hardmetals. A common composition is WC with a Co binding phase. However, the corrosion properties of cobalt are rather poor, and it is preferably replaced by an alloy of Co and Cr or an alloy of Ni, Cr and possibly some other elements for application under corrosive conditions.

These coatings are among the best at resisting abrasion and erosion possibly combined with corrosion. With modern high-velocity flame spraying (HVOF) denser and better coatings are obtained.

- *Conversion coatings*. This group comprises phosphate, chromate and oxide coatings. Phosphate treatment of steel is usually carried out by exposing the steel surface to phosphoric acid containing phosphates of Zn and Mn, either by spraying or by dipping after prior acid pickling or blast cleaning.

Phosphate coatings that are only 1-10  $\mu$  m thick do not provide a complete protection by themselves, and the process is mainly used as pre-treatment before painting or treatment with wax or oil.

Metals such as Zn, Cd, Al and Mg can also be phosphated. Chromate treatment has been widely used on non-ferrous metals, particularly Al and Zn, sometimes as the only treatment and sometimes as pre-treatment before painting. Since chromates are highly toxic the environmental regulations connected with chromate processes have become more stringent, and several efforts have been made to find more environment-friendly conversion alternatives. Oxidation of steel by dipping in hot concentrated alkaline solutions containing persulphates, nitrates and chlorates is used as a base for oil and wax. An important process is oxidation of aluminium and aluminium alloys. It is achieved by anodic polarization, and is usually called anodizing.

The oxide film can be dyed in the anodizing process by various additions to the bath, or it can be dyed afterwards. It is sealed by treatment in boiling water, steam or possibly in a hot, dilute chromate solution. Anodizing provides in itself some improvement of the corrosion resistance of aluminium, and furthermore it gives a good base for painting.

### ***Paint Coatings***

The use of paint coatings is the most common method for corrosion prevention.

- *Compositions and types of paint.* An anticorrosive paint is composed of a binder, pigments, a solvent/diluent, extenders and a variable number of other additives such as antioxidants, surface-active agents, driers, thickeners and antisetling agents. A paint is primarily characterized by its pigment or by its binder. We distinguish between primers, which usually contain pigments

causing some inhibition or cathodic protection of the substrate, and paints for finishing coats, which contain colour pigments and extenders, which may improve the barrier effect of the coating system. The coats in thicker paint systems may be divided into primer, intermediate or body coats and topcoat. Recent development of thick film paints implies less need for distinction between intermediate coats and topcoat.

An actual inhibiting type of pigment in primers is zinc phosphate, while red lead and zinc chromate, which were earlier in widespread use, are seldom applied nowadays because of the risk of health injuries. Metallic zinc powders provide cathodic protection of the substrate if the zinc concentration is high enough. The pigments in the finishing coats provide colour and protect the binder from being damaged by ultraviolet sunlight. The most efficient barrier-acting pigment consists of aluminium flakes.

The aluminium flakes increase the length of the diffusion path and are therefore assumed to increase the resistance to diffusion of water, oxygen and ions, but more recent investigations have shown that the effect and the mechanism depend strongly upon the type of binder. Other commonly used pigments in intermediate coats and topcoats are various forms of iron oxide. The binder may, for instance be bitumen (coal tar or asphalt), or linseed oil (natural materials), alkyd, chlorinated rubber, epoxy, vinyl, polyurethane etc. (synthetic organic materials), or silicate (inorganic). Some paints are hardened by reaction with oxygen in the air (oil and alkyd paints), others by evaporation of the solvent (e.g. chlorinated rubber) and a third group by a chemical reaction between two components (epoxy and polyurethane paints). Recently, a binder of polysiloxane has been introduced. There is also a growing interest for application of water-based paints, e.g. in marine environments.

- *Properties and selection of paint systems* for protection of steel in various environments. The primary questions that have to be asked before selecting a paint system are:

- Which pre-treatment is possible, and what will the condition of the substrate be before painting?
- How will the environment around the painted structure change during various periods of the lifetime? Which mechanical and chemical attacks will the coating be exposed to?
- What are the conditions for application and drying/hardening of the paint, particularly the temperature and the humidity?
- What are the initial and maintenance costs of paint and painting work?

Several so-called rust-stabilizing or rust-converting products are commercially available, but the practical efficiency of these products depends on the conditions.

They are made for coating on rusty substrates, but it is still important to remove loose rust, which can be done by thorough steel brushing. Some products are based on phosphoric acid. These must be applied in appropriate thickness, and excessive acid must be washed away with fresh water before the coating is overpainted.

### ***Other Forms of Organic Coatings***

Rubber coatings provide excellent corrosion protection in seawater and several chemicals, and are used internally in tanks and pipelines. Externally on buried pipelines, asphalt or coal tar has commonly been used, often reinforced with a textile or mineral net, and during the last generation, also tape made from materials such as polyvinyl chloride or polyethylene with adhesive and primer on one side.

Various factory methods for direct application of polyethylene or powder epoxy coatings on pipelines have been developed and used. During the last few decades, glass-flakefilled unsaturated polyester or vinyl-ester coatings have been applied to an increasing extent, particularly on offshore installations, on ships and in industry. These are fasthardening coatings with high mechanical wear resistance and with good ability to protect against corrosion in most environments. The coatings are applied by highpressure spraying in 1-2 coats giving a thickness of 0.75-1.5 mm.

Depending on the environment, all the mentioned types of coating can be combined with cathodic protection to prevent corrosion in/at coating defects.